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Infrared reflectance absorption spectroscopy (IRRAS). Study of the thermal stability of perfluorinated sulphonic acid ionomers on Pt

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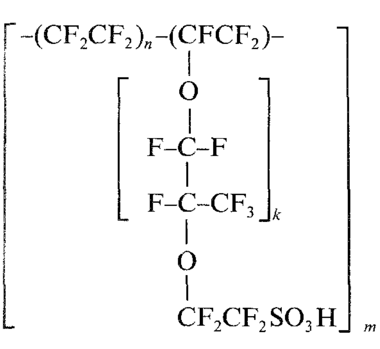
Infrared Reflectance Absorption Spectroscopy (IRRAS) has been used to study the thermal stability of Nafion (du Pont, equivalent weight = 1 100) and a similar perfluorinated sulphonic acid ionomer (PFSI) made by the Dow Chemical Company (equivalent weight = 560). Purified aqueous PFSI electrolytes solutions were prepared, PFSI films (0.5–5 μm) were cast from these aqueous PFSI solutions onto Pt foil substrates for spectral study after heating at various temperatures. Spectra were recorded at room temperature in a vacuum after a film on Pt had been heated at a particular temperature in the presence of air. The temperature range was 22–300° C. Spectral changes for a PFSI film on Pt were not significant when heated at up to 200° C in an air atmosphere; however, when heated at 300° C there was a significant decrease in intensity for S–O related bands indicating substantial loss of the sulphonic acid groups from these ionomers.

1. Introduction

Perfluorosulphonic acid ionomer (PFSI) electrolytes, such as Nafion (du Pont) and similar ionomers produced by the Dow Chemical Co., are gaining increasing attention as surface films on chemically modified electrodes (CME's) [1–7]. A PFSI electrolyte can be made to coat an electrode surface by applying a PFSI solution over the electrode. The PFSI in the solution is formed into an immobilized solid polymer electrolyte (SPE) film on the electrode surface by evaporating the solvent. The PFSI-coated electrode may or may not be further modified by ion-exchanging a cation for the proton associated with the sulphonic acid groups. The structural formulae for these ionomers is



$$\left[\begin{array}{c} -(CF_2CF_2)_n-(\underset{|}{C}FCF_2)- \\ \left[\begin{array}{c} O \\ | \\ F-C-F \\ | \\ F-C-CF_3 \end{array}\right]_k \\ | \\ O \\ | \\ CF_2CF_2SO_3H \end{array}\right]_m$$

in which k is 1–3 for Nafion and 0 for the Dow ionomer.

In the authors' [8, 9] and other [10] laboratories, there is considerable interest in replacing the conventional fluid electrolyte such as concentrated H_3PO_4 with a SPE such as that made from a PFSI in Pt-catalyzed porous air cathodes in order to improve the performance of these electrodes for fuel cell applications. The rationale is that the O_2 reduction reaction may proceed with less polarization at the Pt/PFSI interface than at the Pt/fluid concentrated H_3PO_4 electrolyte interface. The bulk electrolyte between the anode and cathode of the fuel cell would still be concentrated H_3PO_4. The polymer would then be infused with concentrated H_3PO_4.

Oxygen reduction polarization at porous Pt-catalyzed air cathodes has been found to be lower with perfluorinated electrolytes [11, 12] as well as with mixtures of perfluorinated electrolytes plus concentrated H_3PO_4 [13]. Recently, Razaq *et al.* [14] have reported an improved performance for a Pt-catalyzed air cathode using 0.5 wt% of a perfluorosulphonimide as an additive to the 85% H_3PO_4 aqueous electrolyte system. This improvement has been attributed to several factors including the formation of a physically adsorbed layer of the liquid perfluorinated sulphonimide electrolyte on Pt with the fluorocarbon portion of the sulphonimide adjacent to the electrode surface. Within the adsorbed layer, O_2 is expected to have higher concentration than in concentrated H_3PO_4. This and the lower dielectric constant adjacent to the Pt surface within the adsorbed layer favours the competitive adsorption of O_2 relative to other more polar species of the electrolyte. This corresponds to the so-called 'dry cave' effect [14].

Perfluorinated electrolytes could also improve the distribution of the electrolyte within the electrode promoting better contact of the Pt with the electrolyte which results in better utilization of the Pt catalyst [15].

In addition to the possible advantages found when using liquid perfluorinated electrolytes, further

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benefits expected when using a PFSI-SPE as the electrolyte phase in micropore structures of the Pt-catalyzed electrode with concentrated H_3PO_4 as the bulk electrolyte include: (1) immobilization of the electrolyte thus minimizing the redistribution of the electrolyte within the electrode structures during long term operation, (2) extention of the Pt catalyst life by slowing the dissolution/migration loss mechanism of Pt and (3) reduction of surface area loss for Pt. The loss of Pt surface area would be expected to be minimized by arresting one or more of the three following mechanisms by which area loss may occur: (a) detachment of Pt from the carbon substrate and the subsequent agglomeration and sintering of the Pt crystallites, (b) surface migration of Pt atoms on the carbon supports from smaller particles to larger particles with the smaller particles eventually disappearing, and (c) conventional Oswald solution ripening in which small particles dissolve and eventually disappear whereas large particles grow.

With the PFSI-SPE restricted to the electrode and with concentrated H_3PO_4 as the bulk electrolyte, the ohmic loss would be expected to be minimal, in contrast to the significant additional ohmic loss typically encountered when using liquid or solid perfluorinated electrolytes as the bulk electrolyte. Significant loss of the PFSI electrolyte by vaporization it is not expected, because PFSI electrolytes have high molecular weights.

If a PFSI-SPE is to be useful for fuel cell applications, it must be able to withstand the electrode fabrication or at least the fuel cell operation conditions without decomposing. Typical operating conditions for the concentrated H_3PO_4 fuel cell would require the PFSI to be in contact with concentrated H_3PO_4 at 200° C, Pt at 0.7–0.8 V versus RHE and up to several atmospheres of air as well as possible traces of peroxide and oxygen containing radical species. In the fabrication of Teflon (du Pont) bonded electrodes, the electrodes are ordinarily exposed to temperatures on the order of 300° C [16], principally to promote the sintering of the polytetrafluoroethylene (PTFE) particles and to destroy or remove any surfactants which may have been associated with the PTFE.

This study has been carried out as a first step to investigate the thermal stability of PFSI electrolytes on Pt in an oxidizing atmosphere. *Ex situ* infrared reflectance absorption spectroscopy (IRRAS) has been used to examine the spectral changes for the PFSI films cast onto a smooth Pt substrate after heating at different temperatures. Spectra were recorded at room temperature in a vacuum each time after a film on Pt had been heated at a particular temperature in the presence of air. The temperature range was 22–300° C. The PFSI films on Pt were found to be relatively stable up to at least 200° C but decomposed significantly at 300° C when heated in this way.

2. Experimental

High purity (99.998%, Puratronic grade, Johnson Matthey) platinum foils 5 cm^2 (2.5 cm × 2 cm) in area were used. The Pt was pre-cleaned by annealing the foil in a gas/air flame, then plunging the red-hot foil into concentrated aqueous HNO_3 (70 wt%), Fisher reagent grade), followed by rinsing with copious amounts of water purified by reverse osmosis and distillation. A polymer film was made by evaporating a known volume of a PFSI solution onto the pre-cleaned Pt. The film thickness was calculated assuming that the density of a PFSI is 1.98 $g\,cm^{-3}$ [17] and that the film is uniform.

The solutions used for making PFSI films on the Pt foil substrates for the PFSI thermal stability studies were a 3 wt% solution of Nafion (equivalent weight = 1 100) in water and a 2 wt% solution of the Dow PFSI (equivalent weight = 560) in water. The 3 wt% aqueous Nafion solution was prepared from a commercial solution, which is 5 wt% of the proton form of Nafion dissolved in 90% lower aliphatic alcohols, principally isopropanol, and 10% water, and which is available from Solution Technologies, Inc.

The preparation of the aqueous Nafion solution was as follows. The 5 wt% commercial Nafion solution was placed in a dialysis bag (Arthur H. Thomas Company, Cellulose No. 3787-D22). Then the solution filled bag was soaked in purified (reverse osmosis-distilled) water for 1 week during which the water was changed several times per day. The bag was further soaked for 1 more week during which the water was continuously changed as well as warmed between 80–90° C. The solution was removed from the dialysis bag and purified by adding concentrated H_2O_2 (50%, Hach ultrapure grade) to the aqueous Nafion solution until the H_2O_2 concentration was 1 M. This mixture was warmed at 80–90° C for several hours after the cessation of bubble evolution. A Pt foil electrode was placed in the Nafion solution and cycled between 0.05–1.5 V versus NHE to remove any residual peroxide. The purified aqueous solution had a concentration of approximately 3 wt% Nafion. The concentration was determined by evaporating the water from a known volume of the solution in a preweighed container at 120° C and then weighing to determine the mass of the dried Nafion.

The aqueous Dow PFSI solution was prepared from a membrane received in the sodium form. The membrane was converted to the proton form by soaking it in dilute perchloric acid (1 part 70 wt% Baker reagent: 1 part water) with ultrasonic agitation for 1 h. The perchloric acid was diluted ten fold, further agitated for 15 min and then decanted. This ion-exchanging procedure was repeated. The membrane was then soaked in reverse osmosis purified water with ultrasonic agitation for 15 min and then the liquid was decanted away. This soaking procedure was repeated three times. In order to remove oxidizable impurities from the membrane, it was soaked in concentrated H_2O_2 (50%, Hach ultrapure grade) with sonication for 1 h, and then water was added to dilute the peroxide to $\sim 5\%$, and the membrane was soaked overnight in this dilute H_2O_2 solution with stirring and warming at $\sim 60°$ C. The H_2O_2 solution was decanted away, and the membrane was then further cleansed by soaking several times in fresh reverse osmosis purified water using ultrasonic agitation over 1 h.

The 2 wt% Dow 560 PFSI/H_2O solution was made from the Dow PFSI membrane in a manner similar to that reported for the preparation of alcohol solutions of Nafion from Nafion membranes [18]. A 1.5 g piece of the Dow 560 PFSI membrane was dissolved in 75 ml of water by heating for 10 min at 250° C and 550 psi in Parr model 4561 pressure vessel. The PFSI/water solution was purified by the H_2O_2 and H_2/Pt black treatment [19]. Concentrated H_2O_2 solution was added to the PFSI/H_2O solution until the concentration of H_2O_2 was 1 M. The mixture was heated at 60° C overnight. The mixture was brought to room temperature; 0.1 g of Pt black (Englehard, fuel cell grade) was added. H_2 gas (Matheson, 99.999%) was passed through this mixture for 4 h. The Pt black was removed by filtering through a 1 μm filter (Millipore, polycarbonate) under a H_2 atmosphere. The concentration of this aqueous Dow PFSI solution was determined by the gravimetric method used for the aqueous Nafion solution.

The commercial alcoholic Nafion solution and an alcohol based Dow 560 PFSI solution were also used to make PFSI films on Pt for comparison to those made from the aqueous PFSI solutions. The Dow 560 PFSI/isopropanol solution was 0.5 wt% and was made by dissolving 0.050 g of the purified membrane in 10 ml of isopropanol (Fisher reagent grade) using ultrasonic agitation for 1 h at room temperature and pressure.

Spectral measurements were made using an IBM Instruments IR-98AF Fourier transform infrared spectrometer with a liquid N_2 cooled mercury cadmium telluride (MCT) detector. The spectral resolution was 2 cm^{-1}. Each reported spectrum is the signal average of 200 or more replicate spectra.

For the infrared reflectance absorption spectroscopic (IRRAS) [20] measurements, a PFSI film on Pt was heated in air, transferred to the spectrometer sample chamber, and the spectra were obtained with the sample in the evacuated chamber at room temperature. The absorption spectra of the PFSI film were obtained by ratioing the infrared radiation reflected from the film-coated Pt surface to the infrared radiation reflected from the bare Pt reference surface under the same conditions. The reflectance spectra from the bright Pt surface ratioed to throughput radiation gave a relatively flat baseline with no noticeable absorption bands in the observed spectral window between 4 000 to 600 cm^{-1}.

3. Results and discussion

The transmission spectrum of a 0.5 μm film cast from the 2 wt% aqueous Dow 560 PFSI solution onto a transparent KRS-5 salt plate at room temperature is given in Fig. 1. This spectrum is similar to that of a PFSI film prepared from Nafion [21]. The characteristic PFSI absorption bands are: 1 350 to 1 250 cm^{-1} due to asymmetric S–O stretching modes, 1 250 to 1 150 cm^{-1} due to C–F stretching modes, 1 100 to 950 cm^{-1} due to C–O–C and S–O symmetric stretching modes, and 700 to 600 cm^{-1} due to the C–S stretching and C–F bending modes. The absorption at 985 cm^{-1} attributed to the Nafion C–O–C stretching mode is not found with the Dow PFSI, because this ether linkage is absent in the Dow ionomer (*k* is 0 in the structural formula for the Dow ionomer). No additional bands are observed indicating no major impurities in the Dow 560 PFSI/H_2O solution.

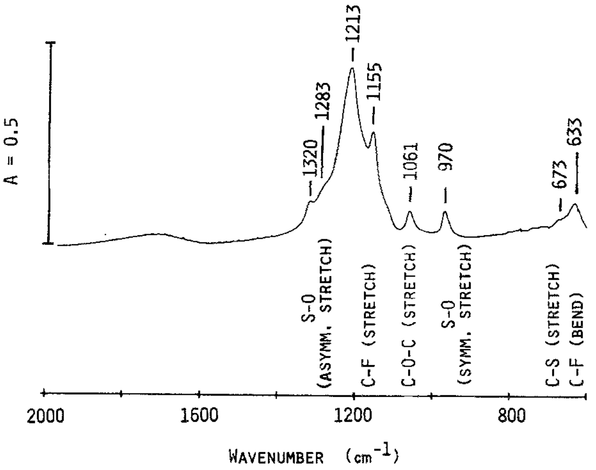

Fig. 1. Infrared absorption spectrum of an unheat-treated 0.5 μm Dow 560 PFSI film cast at 22° C from aqueous solution onto a KRS-5 salt plate. Spectrum sampled in the transmission mode in a vacuum at room temperature.

The same aqueous Dow polymer solution was used to cast a film on Pt. Figure 2 shows the IRRAS spectrum for a 5 μm Dow 560 PFSI film cast and dried at 22° C on Pt and also the spectrum after this sample was heated at 300° C for 7 h in air. The infrared spectra were obtained in vacuo at room temperature. The angle of incidence of the unpolarized infrared beam was 45°. Under these conditions, the reflectance absorption spectrum is dominated by absorption from

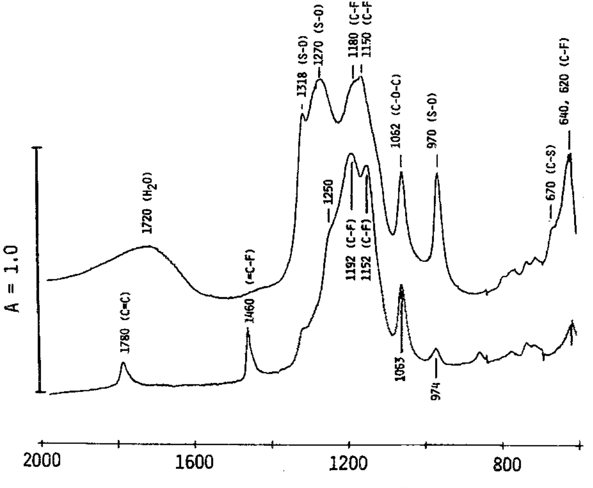

Fig. 2. Infrared reflectance absorption spectra (IRRAS) of a 5 μm thick Dow 560 PFSI electrolyte film on Pt in vacuo at room temperature. Angle of incidence of the unpolarized radiation = 45°. Top spectrum: no heat treatment. Bottom spectrum: after heating the sample at 300° C for 7 h in air.

the bulk polymer phase but also has some smaller contribution from the Pt/polymer interphase. The spectrum of the Dow 560 PFSI film on Pt taken after heating at 300° C in air is considerably different from the spectrum of the unheat-treated sample. The absorption bands at 1318 and 1270 cm^{-1} receded significantly after the heating at 300° C in air. These bands occur in the region associated with the S–O stretching modes, and their receding suggests that most of the $-SO_3H$ groups were lost from the PFSI film. This is consistent with the infrared studies of thermal effluents reported by du Pont which indicate stoichiometric quantities of SO_2 are lost from Nafion when a Nafion 117 membrane is heated at 270° C in a stainless steel vessel in the presence of air [22].

The shoulder found at ~ 1250 cm^{-1} after the heat treatment may have been present for the spectrum of the unheat-treated sample, but was obscured by the strong S–O peak at 1270 cm^{-1}. This shoulder is probably attributable to a C–F absorption band [23], but it could also be due to a residual $-SO_3H$ band or to adsorbed or occluded SO_2 generated during the decomposition. The strong bands found between 1200 and 1150 cm^{-1} correspond to C–F stretching vibrations and are essentially insensitive – as is expected – to the heat treatment.

As a result of the heat treatment, there was a significant lessening in intensity of the distinct shoulder at ~ 670 cm^{-1} attributed to the C–S stretching vibration, and this suggests the C–S bond linking the $-SO_3H$ group onto the polymer was broken during the heating. Two bands at 620 and 640 cm^{-1} overlap the band at 670 cm^{-1}. These bands have been attributed to C–F bending in two different helical arrangements of the fluorocarbon skeleton [24]. Intensity for the C–F bands at 640 and 620 cm^{-1} the C–F bending modes are reported to be temperature sensitive [24]. The apparent decrease in intensity of these bands after the heat treatment is probably not a sign of decomposition of the fluorocarbon skeleton, but rather is tentatively attributed to the effects of increasing helix reversal as well as loss in intensity of the overlapping C–S band at 670 cm^{-1} as a result of heat treating the film.

The band at 1063 cm^{-1} which is supposed to be associated with the S–O symmetric stretching vibration [21] was not affected by the heat treatment. Therefore the 1063 cm^{-1} band is probably not related to the $-SO_3H$ substitutent but instead may be associated with the C–O–C vibration. The band at -970 cm^{-1} usually associated with the C–O–C vibration [21] was found to lessen in intensity after heating. This suggests either that the C–O–C ether linkage had been broken, or alternatively – and more likely – that 970 cm^{-1} band is the absorption due to the S–O symmetric stretch which should lessen in intensity as $-SO_3H$ groups are lost.

After the 300° C heat treatment, new bands at 1780 and 1460 cm^{-1} appeared. Unsaturated C–C or carboxylate C–O groups are expected to be present after perfluorocarbon polymers decompose via elimination reaction pathways [25]. The band at 1780 cm^{-1} is probably associated with a C = C vibration [26], and the band at 1460 cm^{-1} is probably associated with a C–F vibration from a $-C=CF_2$ group. A carboxylate fragment could, however, account for the both of these bands [27]. Assuming the intensities of the S–O bands at 1318 and 970 cm^{-1} and the C–S band at 670 cm^{-1} are proportional to the number of $-SO_3H$ groups, the intensities of these bands are useful for estimating the degree of decomposition. Changes in peak intensities with heating time indicate that the decomposition process at 300° C was less than 30% completed after one hour and was over 90% completed after 7 h for this relatively thick film.

When a PFSI is loaded into a Pt-catalyzed porous air cathode, the thickness of the PFSI film on Pt is expected to be on the order of 1 μm or less, and therefore the stability of thinner (0.5 μm) PFSI films cast on Pt were also studied. When radiation is reflected from a metallic surface, the intensity at the surface for the electric field for the *s*-polarized component approaches zero, but the intensity at the surface for the *p*-polarized component is increased relative to the incident radiation. The intensity of the *p* component may be several fold greater than the incident radiation when reflected at an angle of 75 to 88° [see for example, References 20, 28, 29]. Therefore the sensitivity and the signal to noise ratio for an absorption spectrum of a thin film of a metallic surface are considerably improved using *p*-polarized radiation reflected at a high angle of incidence.

The spectra of a 0.5 μm film of the Dow 560 PFSI electrolyte cast from purified aqueous solution onto Pt foil were obtained using *p*-polarized radiation with a 75° angle of incidence. The spectra of the sample were obtained at room temperature under vacuum each time after the same film on Pt had been heated at 110, 160, 200 and 300° C in air for 15 min (see Fig. 3). There were no significant differences in the spectra until the

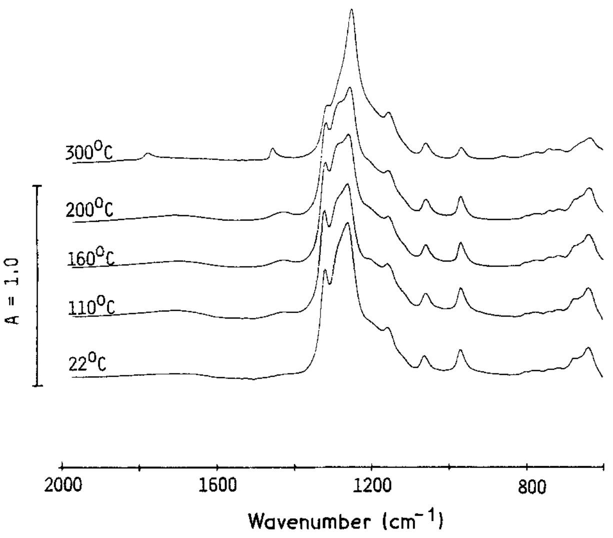

Fig. 3. Infrared reflectance absorption spectra (IRRAS) of a 0.5 μm thick Dow 560 PFSI film on Pt sampled in a vacuum at room temperature. Angle of incidence of *p*-polarized radiation = 75°. Bottom spectrum: no heat treatment. Next to bottom through to the top: sample heated for 15 min in air at 110, 160, 200 and 300° C before the spectrum was taken.

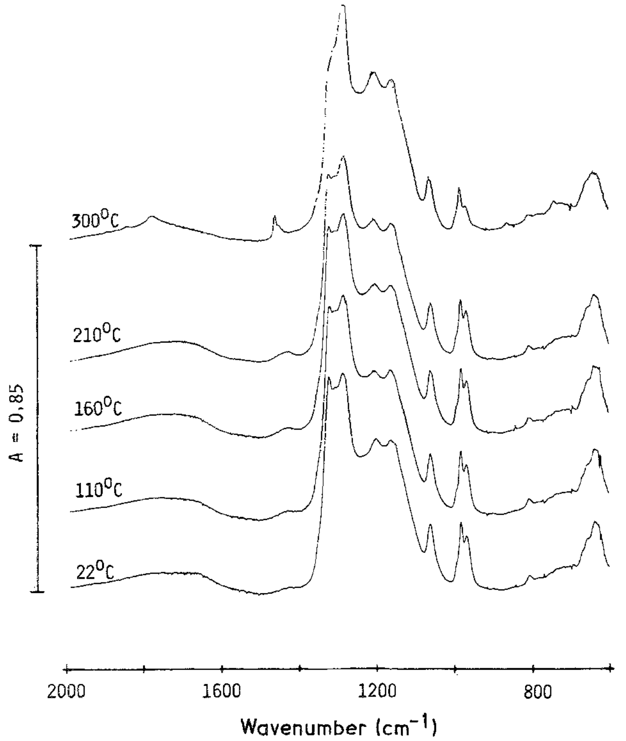

Fig. 4. Infrared reflectance absorption spectrum (IRRAS) of a 0.6 μm thick Nafion film on Pt sampled in a vacuum at room temperature. Angle of incidence of *p*-polarized radiation = 75°. Bottom spectrum: no heat treatment. Next to bottom through to the top: sample heated for 15 min at 110, 160, 210 and 300° C in air before the spectrum was taken.

sample was heated at 300° C. The spectral changes were symptomatic of $-SO_3H$ loss from the film. These spectral changes are analogous to those found for the relatively thick film shown in Fig. 2.

Similar thermal stability studies were carried out for Nafion on Pt. A 0.6 μm film of Nafion was cast from the purified 3 wt% aqueous Nafion solution onto Pt. The spectra shown in Fig. 4 were obtained after the sample was heated at 110, 160, 210 and 300°C for 15 min. The spectra were obtained in vacuo at room temperature. The angle of incidence of the *p*-polarized radiation was 75°. Again there were no changes in the spectra until the sample was heated at 300° C. The significant loss of intensity for the bands at 1325, 970 and 670 cm^{-1} and the appearance of the bands at 1790 and 1460 cm^{-1} after heating the film at 300° C indicates the loss of $-SO_3H$ groups. Apparently the Nafion and Dow PFSI films have the same stability under the conditions studied here.

Spectra of the Nafion and Dow PFSI films carefully cast from alcoholic solutions onto Pt were similar to those cast from water solutions. For example, a 0.6 μm film of Nafion was case from the commercial alcohol solution onto Pt. The film was made by quickly spreading 12 μl of the alcoholic Nafion solution over the surface of the Pt foil at room temperature. Within a minute, most of the solvent evaporated, and the remaining polymer solution congealed. The sample was then immediately transferred to a tube furnace where it was thoroughly dried under a He atmosphere at 95° C for ~15 min. The reflectance absorption spectrum was measured in vacuo at room temperature. The angle of incidence of the *p*-polarized radiation was 75°. The spectrum for the Nafion film cast from the alcohol solution onto Pt was found to be virtually identical to the spectrum shown in Fig. 4 for the Nafion film cast from aqueous solution onto Pt. This indicates the chemical composition for the Nafion found in alcohol and water solutions is similar. Furthermore, since no additional bands were found in the spectrum of the Nafion film cast from the alcoholic solution onto Pt in this way, it would seem that there were no appreciable amounts of nonvolatile impurities in this solution nor were there the appreciable amounts of alcohol decomposition products formed. Nonetheless, care must be taken whenever treating Pt electrodes with alcoholic PFSI solutions, so as not to poison the Pt with alcohol decomposition products [30].

Infrared reflectance absorption spectroscopy using *p*-polarized radiation at grazing incident angles has enhanced sensitivity to the metal/adsorbate interphase within a fraction of a wavelength of the interface [28, 29]. As a result of the so-called 'surface selection rule' [31], the vibrational modes which have oscillating dipoles normal to and at the metal surface are the most intense absorbers. The ratio of the intensities of the $-SO_3H$ bands to C–F bands is apparently greater in the IRRAS spectrum of the 0.5 μm Dow PFSI film on Pt (shown in Fig. 3) compared to the transmission spectrum of the 0.5 μm film on KRS-5 (shown in Fig. 1). This difference in the ratio of the intensities of the $-SO_3H$ versus C–F bands between the IRRAS spectrum and the transmission spectrum suggests the existence of a preferred orientation of the sulphonic acid groups toward the Pt surface possibly due in part to a specific interaction between the sulphonic acid group and the Pt surface.

A specific interaction such as between the $-SO_3H$ groups (but not C–F portion) of the PFSI and Pt, however, is only one factor which can influence the appearance of the infrared spectra. Optical and non-specific surface effects must also be carefully considered before infrared absorption spectroscopy can be expected to yield reliable information about the interaction or orientation of polymers toward surface [32–34]. Further spectral studies concerning PFSI/substrate interactions are in progress and may further elucidate the nature of the surface selectivity of the PFSI moieties [35].

4. Summary

This study was a first step in examining the stability of PFSI electrolytes exposed to conditions similar to those found during the operation and preparation of PFSI modified electrodes for the H_2/O_2 acid fuel cell.

The PFSI films appear to be stable when used at elevated temperatures (up to 150° C) during O_2 polarization measurements on Pt in concentrated H_3PO_4 [8–10]. The IRRAS data shows that the PFSI electrolytes are thermally stable below 200° C when a dry

PFSI film on Pt is heated in air for short times. When a PFSI film is impregnated with a proton solvating agent such as phosphoric acid, the PFSI film is expected to be stable up to 200° C, or perhaps even higher temperatures for extended periods of time. This is the subject of ongoing studies.

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